



## SPECIFICATION

## Separation membrane and separation method

(1) A separation membrane for separating an organic solvent mixture, wherein an acrylic monomer is plasma graft-polymerized on a microporous membrane composed of ultra-high-molecular-weight polyethylene having a thickness of 0.1 to 50  $\mu\text{m}$ , a porosity of 30 to 95%, an average pore diameter of 0.005 to 1  $\mu\text{m}$ , a break strength of 200  $\text{kg}/\text{cm}^2$  or more and a weight average molecular weight of  $5 \times 10^5$  or more, thereby, a pore of the microporous membrane is substantially choked with an acrylic graft polymer.

(2) The separation membrane according to claim 1, wherein the graft polymer for choking the pore is polymethyl acrylate.

(3) A method of separating an organic solvent mixture, which comprises selectively separating an organic solvent having the affinity with an acrylic graft polymer by a pervaporization method or a reverse osmosis method, using a separation membrane obtained by plasma graft-polymerizing an acrylic monomer on a microporous membrane composed of ultra-high-molecular-weight polyethylene having a thickness of 0.1 to 50  $\mu\text{m}$ , a porosity of 30 to 95%, an average pore diameter of 0.005 to 1  $\mu\text{m}$ , a break strength of 200  $\text{kg}/\text{cm}^2$

or more and a weight average molecular weight of  $5 \times 10^5$  or more, thereby, a pore of the microporous membrane is substantially choked with an acrylic graft polymer.

(4) The method of separating an organic solvent mixture according to claim 3, wherein the graft polymer for choking the pore is polymethyl acrylate and benzene is separated from the organic solvent mixture containing benzene and cyclohexane.

### 3. Detailed Description of the Invention

#### [Industrial field of application]

The present invention relates to a membrane for separating an organic solvent mixture and a separation method, in particular, a separation membrane that can be suitably used for separating an organic solvent having the higher affinity with an acrylic polymer from an organic solvent having the lower affinity with an acrylic polymer, and a separation method using the separation membrane.

#### [Prior art and Problems that the invention to be solved]

A membrane separation method of separating various mixtures using a membrane having a pore has recently become increasingly popular, and such the technique is being applied in a variety of fields. In addition, the membrane separation method separates not only a solid-liquid mixture, but also a wide range of a liquid-liquid mixture, a gas-gas mixture and a gas-liquid mixture, and an attention is focused on the development of a separation membrane and a separation technique handling a variety of

mixtures.

Separation of an organic solvent by the membrane separation method is one of the fields of interest, and is being studied as a method of separating or concentrating a mixture which could not be previously separated by the simple method (for example, a mixture which is difficult to be separated by distillation due to close boiling points of organic solvents, an azeotropic mixture, a mixture containing heat-labile substances, and the like). A pervaporization method and a reverse osmosis method are preferable in a membrane method of separating a mixture of organic solvents.

Meanwhile, since accuracy and an efficacy of separation in the membrane separation method including a pervaporization method and a reverse osmosis method depend on a performance of a membrane itself, it is important to develop a membrane excellent in the strength, the durability and the separation selectivity, and various polymer membranes have been previously proposed.

For example, Japanese Patent Application Laid-Open (JP-A) No. 50-98568 discloses a permeation membrane in which a polymerizable monomer is graft-polymerized on the surface in a pore of a high-molecular polymer film having a pore. This permeation membrane uses, as a substrate, a high-molecular polymer film having a pore such as polyethylene excellent in the durability, the heat resistance and the chemical resistance, in which a

polymerizable monomer having the affinity with a subject to be separated is graft-polymerized on the surface of a pore. Although this separation membrane is suitable for separating an aqueous mixture by a reverse osmosis method, the membrane has not a sufficient performance in separation of an organic solvent mixture such as a benzene/cyclohexane mixture.

Further JP-A No. 52-122279 discloses a separation membrane made of an aliphatic olefin polymer having an acid group derived from an unsaturated carboxylic acid and the like. In this separation membrane, an unsaturated carboxylic acid or the like is polymerized on the surface of a membrane substrate made of an aliphatic olefin polymer or the like by a cross-linking reaction by a radical reaction, light irradiation or electron beam irradiation. This separation membrane can be used in a pervaporization method and, in particular, can relatively easily separate an unsaturated compound from a mixed solution of organic solvents. However, this membrane is used by placing on a porous support, and is not yet actually sufficient in a performance of a membrane.

For obtaining an excellent separation membrane, it is fundamentally necessary to selectively enhance the affinity with a compound to be separated. However, when a whole separation membrane is made of a material having the affinity with a component of interest, a separation membrane is swollen, thereby, high separation selectivity

can not be obtained due to plasticizing effect. In addition, there arise problems of reduction in the mechanical strength and the durability of a separation membrane.

Therefore, an object of the present invention is to provide a separation membrane which can separate a mixture composed of organic solvents such as a benzene/cyclohexane mixed solution with high selectivity, and is also excellent in the strength and the durability.

In addition, another object of the present invention is to provide a separation method having high selectivity to an organic solvent mixture.

[Means to solve the problems]

In view of the aforementioned object, the present inventors intensively studied and, as a result, found that using a microporous membrane of ultra-high-molecular-weight polyethylene having a specified porosity and a specified average pore diameter, an acrylic monomer is plasma graft-polymerized on this membrane to obtain a separation membrane in which a pore is substantially choked with an acrylic graft polymer, whereby, there is obtained a separation membrane through which an organic solvent having the affinity with an acrylic graft polymer is permeated and which is also excellent in the strength and the durability, which resulted in completion of the present invention.

That is, the separation membrane of the present invention used in separation of an organic solvent mixture

is characterized in that an acrylic monomer is plasma graft-polymerized on a microporous membrane composed of ultra-high molecular-weight polyethylene having a thickness of 0.1 to 50  $\mu\text{m}$ , a porosity of 30 to 95%, an average pore diameter of 0.005 to 1  $\mu\text{m}$ , a break strength of 200  $\text{kg}/\text{cm}^2$  or more and a weight average molecular weight of  $5 \times 10^5$  or more, thereby, the pore of a microporous membrane is substantially choked with an acrylic graft polymer.

In addition, the method of the present invention of separating an organic solvent mixture is characterized in that an organic solvent having the affinity with an acrylic graft polymer is selectively separated by a pervaporization method, using a separation membrane obtained by plasma graft-polymerizing an acrylic monomer on a microporous membrane composed of ultra-high-molecular-weight polyethylene having a thickness of 0.1 to 50  $\mu\text{m}$ , a porosity of 30 to 95%, an average pore diameter 0.005 to 1  $\mu\text{m}$ , a break strength of 200  $\text{kg}/\text{cm}^2$  or more and a weight average molecular weight of  $5 \times 10^5$  or more, thereby, the pore of a microporous membrane is substantially choked with an acrylic graft polymer.

The invention will be described in detail below.

First, the separation membrane of the present invention will be explained.

The separation membrane of the present invention has a substrate composed of an ultra-high-molecular-weight polyethylene microporous membrane. Ultra-high-molecular-

weight polyethylene which is used as a material for the substrate is crystalline linear ultra-high-molecular-weight polyethylene composed of a homopolymer of ethylene or a copolymer of ethylene and 10 mol% or smaller of  $\alpha$ -olefin. A molecular weight thereof is such that a weight average molecular weight is  $5 \times 10^5$  or more, preferably  $1 \times 10^6$  to  $1 \times 10^7$ . A weight average molecular weight of ultra-high-molecular-weight polyethylene has influence on the mechanical strength of the resulting separation membrane. When a weight average molecular weight is smaller than  $5 \times 10^5$ , a separation membrane having the high strength can not be obtained because of an extremely small thickness. On the other hand, an upper limit of a weight average molecular weight is not particularly limited, when a weight average molecular weight exceeds  $1 \times 10^7$ , it is difficult to make a membrane thin by stretching processing, being not preferable.

As an ultra-high-molecular-weight polyethylene microporous membrane, ultra-high-molecular-weight polyethylene incorporating other polyethylene having a relatively low molecular weight can be used. In this case, a polyethylene composition is preferably such that ultra-high-molecular-weight polyethylene having a weight average molecular weight of  $7 \times 10^5$  or more is contained at 1% by weight or more, and weight average molecular weight/number average molecular weight is 10 to 300.

Weight average molecular weight/number average

molecular weight of the aforementioned polyethylene composition is 10 to 300, preferably 12 to 250. When weight average molecular weight/number average molecular weight is less than 10, it is difficult to prepare a highly-concentrated solution, since an average molecular chain length is great, and a density of entanglement of molecular chains at dissolution becomes high. On the other hand, when weight average molecular weight/number average molecular weight exceeds 300, rupture of a low molecular - weight component occurs at stretching, and the strength of a whole membrane is reduced.

Weight average molecular weight/number average molecular weight is used as an index for a molecular weight distribution and, as this ratio of a molecular weight becomes large, a width of a molecular weight distribution is extended. That is, in a composition containing polyethylene having different weight average molecular weights, as a ratio of a molecular weight of the composition becomes larger, a difference in weight average molecular weights of polyethylenes to be incorporated becomes large and, as the ratio becomes smaller, a difference in weight average molecular weights becomes small.

An amount of the ultra-high-molecular-weight polyethylene in a polyethylene composition is 1% by weight or larger based on 100% by weight of a whole polyethylene composition. When an amount of ultra-high-molecular-



polyethylene is smaller than 1% by weight, entanglement of molecular chains of ultra-high-molecular-weight polyethylene contributing to improvement in the stretchability is scarcely formed, and a microporous membrane having the high strength can not be obtained. On the other hand, an upper limit is not particularly limited, but when the amount exceeds 90% by weight, it becomes difficult to attain the high concentration of a polyethylene solution of interest.

Polyethylene other than ultra-high-molecular-weight polyethylene in a polyethylene composition has a weight average molecular weight of lower than  $7 \times 10^5$ , and a lower limit molecular weight is preferably  $1 \times 10^4$  or larger. When polyethylene having a weight average molecular weight of lower than  $1 \times 10^4$  is used, rupture easily occurs at stretching, and a desired microporous membrane is not obtained, being not preferable. It is particularly preferable that polyethylene having a weight average molecular weight of  $1 \times 10^5$  or larger and smaller than  $7 \times 10^5$  is incorporated in ultra-high-molecular-weight polyethylene.

As such the polyethylene, there is the same kind as the aforementioned ultra-high-molecular-weight polyethylene and, in particular, high-density polyethylene is preferable.

To the aforementioned ultra-high-molecular-weight polyethylene microporous membrane both alone or in the form

of a composition may be added, if necessary, various additives such as an antioxidant, an ultraviolet absorbing agent, a lubricant, an anti-blocking agent, a pigment, a dye and an inorganic filler in such a range that the object of the present invention is not deteriorated.

Then, a process for preparing the ultra-high-molecular weight polyethylene microporous membrane will be explained.

First, a microporous membrane composed of ultra-high-molecular-weight polyethylene alone can be prepared by the process described, for example, in JP-A No.60-242035.

Then, a microporous membrane composed of a polyethylene composition incorporating polyethylene having a relatively low molecular weight in ultra-high-molecular-weight polyethylene can be prepared by the following process.

First, the aforementioned polyethylene composition is dissolved in a solvent by heating to prepare a high concentration solution. A solvent therefor is not particularly limited as far as it can sufficiently dissolve the polyethylene composition and the same solvents as those described in JP-A No. 60-242035 may be used. Heating dissolution is performed while stirring at such a temperature that the polyethylene composition is completely dissolved in a solvent. Such the temperature is different depending on a polymer and a solvent used, and a range of 140 to 250°C is preferable. In addition, the concentration

of a polyethylene composition solution is 10 to 50% by weight, preferably 10 to 40% by weight.

Then, the heated solution of this polyethylene composition is molded by extruding through a die. As a die, a sheet die having a rectangular mouthpiece shape is usually used, although a double cylindrical hollow die, an inflation die and the like may be also used. When a sheet die is used, a die gap is usually 0.1 to 5mm, and the material is heated to 140 to 250°C at extrusion molding. Upon this, an extruding rate is usually 20 to 30cm/min. to 2 to 3 m/min.

The solution thus extruded through a die is formed into a gel by cooling. It is preferable that cooling is performed at a rate of 50°C/min. or higher at a gelling temperature or lower.

Then, this molded gel is stretched. Stretching is performed at a prescribed ratio using the conventional tenter method, roll method, inflation method, rolling method or a combination thereof as described above, by heating the molded gel. Biaxial stretching is preferable, either of longitudinal and traverse simultaneous stretching or successive stretching may be used, and simultaneous biaxial stretching is particularly preferable.

A stretching temperature is not less than 10°C or lower over a melting point of a polyethylene composition, preferably in a range of from a crystal dispersion temperature to lower than a crystal melting point, for

example, in a range of 90 to 140°C, more preferably 100 to 130°C.

A thickness of the resulting obtained ultra-high-molecular-weight polyethylene microporous membrane which is to be a substrate of the separation membrane of the present invention is 0.1 to 50  $\mu\text{m}$ , preferably 0.2 to 25  $\mu\text{m}$ . When the thickness is smaller than 0.1  $\mu\text{m}$ , the mechanical strength of a membrane is small, and it is difficult to be subjected to practical use. On the other hand, when the thickness exceeds 50  $\mu\text{m}$ , a thickness is too large, leading to reduction in permeation performance, being not preferable.

A porosity of a microporous membrane is in a range of 30 to 95%, preferably 50 to 90%. When porosity is smaller than 30%, permeability of a subject to be separated is insufficient. On the other hand, when porosity exceeds 95%, the mechanical strength of a membrane becomes lower, being inferior in the practical use.

An average pore diameter is in a range of 0.005 to 1  $\mu\text{m}$ . When an average pore diameter is smaller than 0.005  $\mu\text{m}$ , permeability of a subject to be separated becomes insufficient and, when an average pore diameter exceeds 1  $\mu\text{m}$ , separation performance is reduced.

Further, by making break strength 200kg/cm<sup>2</sup> or larger, deformation resistance to swelling becomes sufficient when a solvent is dissolved in an acrylate graft polymer.

In the separation membrane of the present invention, an acrylic monomer is graft-polymerized at least on the surface of a pore of the aforementioned ultra-high-molecular-weight polyethylene microporous membrane, and the separation membrane has a structure in which a pore is substantially choked with an acrylic polymer. Graft polymerization of an acrylic monomer is performed by a plasma graft polymerization method as described below. As the acrylic monomer, acrylic acid, methacrylic acid, and an ester thereof can be used, and a monomer is appropriately selected depending on a subject to be separated.

When a membrane is a membrane for separating a benzene/cyclohexane mixture, methyl acrylate is graft-polymerized. Polymethyl acrylate has the affinity with benzene, and attempts to be swollen by dissolution of benzene. However, since deformation is suppressed by an ultra-high-molecular-weight polyethylene microporous membrane, dissolution diffusion due to the plasticizing effect of cyclohexane having no affinity is suppressed. For this reason, only benzene passes through a pore, thus, the separation membrane makes benzene among a benzene/cyclohexane mixture selectively permeate. In a pore, swelling of polymethyl acrylate by benzene is suppressed, a whole membrane is scarcely deformed, and the membrane strength is not reduced.

In order to graft-polymerize an acrylic monomer on the surface of a pore of a microporous membrane, a plasma

graft polymerization method is used. In the plasma graft polymerization method, an ultra-high-molecular-weight polyethylene microporous membrane is irradiated with plasma to produce a radical and, thereafter, an acrylic monomer is contacted with the microporous membrane, followed by graft polymerization. As the plasma graft polymerization, there are a vapor phase polymerization method and a liquid phase polymerization method. For graft-polymerizing an acrylic monomer, a liquid phase polymerization method is preferable. Like this, by producing not an acrylic monomer to be graft-polymerized but a radical in a microporous membrane as a substrate to perform graft polymerization, an acrylic monomer can be graft-polymerized even on the surface in a pore. Further, a homopolymer produced thereupon is washed out with a solvent. In addition, a graft polymer is produced also on the surface other than the surface in a pore of the ultra-high-molecular-weight polyethylene microporous membrane, but since this has influence on substantial permeability, it is desirable to reduce this as much as possible.

In Fig. 1 (a), (b-1) and (b-2) are a cross-sectional view conceptionally showing a step of plasma graft-polymerizing an acrylic monomer on an ultra-high-molecular-weight polyethylene microporous membrane 1 to prepare the separation membrane of the present invention. The ultra-high-molecular-weight polyethylene microporous membrane 1 has a large number of pores 2 penetrating the membrane.

Plasma graft polymerization is performed on this microporous membrane to graft-polymerize an acrylic monomer on the surface thereof. A graft-polymerized acrylic polymer 3 is formed not only on the surface part of the microporous membrane but also on the surface in a pore. (B-1) shows one aspect of a membrane in which a pore is substantially filled with a graft polymer 3. In (b-2), a graft polymer 3 is formed on one side of the microporous membrane. Herein, a graft polymer 3 is formed even on a part of a pore, and chokes a pore 2. The separation membrane of the present invention may take any of both structures.

A homopolymer which has been produced as a side product during a process of plasma graft polymerization is completely washed out using a solvent such as toluene and the like, and only a graft polymer is left on the surface of the ultra-high-molecular-weight polyethylene microporous membrane (the surface in a pore and the surface of a membrane).

Plasma graft polymerization comprises specifically the following steps:

(a) In the presence of a gas such as argon, helium, nitrogen, air and the like at a pressure of  $10^{-2}$  to 10 mbar, plasma treatment is performed on a microporous membrane for 1 to 1000 seconds usually at a frequency of 10 to 30 MHz and an output of 1 to 1000 W.

(b) The plasma-treated microporous membrane is

immersed into a solution, in particular, an aqueous solution in which 1 to 10% by weight of an acrylic monomer is dissolved or suspended in an inorganic or organic solvent, and a graft polymerization reaction is performed at 20 to 100°C for 1 to 60 minutes while bubbling a nitrogen gas, an argon gas or the like.

(c) The resulting microporous membrane is washed with toluene, xylene or the like for around 1 hour followed by drying.

The aforementioned plasma graft polymerization method can afford a desired separation membrane in which a pore of a microporous membrane is substantially choked with an acrylic graft polymer. Since plasma graft polymerization occurs only on a surface part of an ultra-high-molecular-weight polyethylene microporous membrane, a membrane substrate is not deteriorated. In addition, since graft polymerization is chemically connected to a membrane substrate, there is no change with time.

In the separation membrane of the present invention, it is required that a pore of a membrane substrate, an ultra-high-molecular-weight polyethylene microporous membrane, is substantially choked with an acrylic graft polymer. An acrylic graft polymer choking a pore selectively takes in a particular component in an organic solvent mixture, and permeates it up to an opposite side of a membrane. Since an ultra-high-molecular-weight polyester microporous membrane has a high porosity, a larger amount



of a substance passes (is separated) through an acrylic graft polymer in a pore, thus, effective separation is possible. In addition, since swelling of an acrylic graft polymer is suppressed by an ultra-high-molecular-weight polyethylene microporous membrane, the strength of a membrane as a whole is not reduced.

Then, a separation method using the aforementioned separation membrane of the present invention will be explained.

In the method of the present invention, an organic solvent mixture is separated by a pervaporization method or a reverse osmosis method using the separation membrane of the present invention which has been described in detail. A pervaporization method or a reverse osmosis method in the method of the present invention is fundamentally the same as the known pervaporization or reverse osmosis method except that the separation membrane of the present invention is used. A primary side and a secondary side are isolated by the separation membrane of the present invention, a mixed liquid to be separated is supplied to a primary side, a secondary side is low-pressure side, and one component of the mixed liquid is taken out as a gas or a liquid to a secondary side. When, for example, a benzene/cyclohexane mixture is separated using, as a separation membrane such an ultra-high-molecular-weight polyethylene microporous membrane on which methyl acrylate has been graft-polymerized, benzene is taken out as a gas

or a liquid to a secondary side.

A range of an applied temperature in the present separation method is usually 0 to 120°C, preferably 10 to 100°C. At a temperature higher than 120°C, the heat resistance of the high-molecular polyethylene microporous membrane becomes insufficient, giving rise to a problem of maintenance of a membrane shape. At a temperature below 0°C, a permeation amount per unit membrane area, membrane thickness and time becomes small, being not preferable.

In addition, a range of a pressure which can be applied to the present method is 200kg/cm<sup>2</sup> or lower, preferably 100 kg/cm<sup>2</sup> or lower. At a pressure exceeding 200kg/cm<sup>2</sup>, it becomes difficult to maintain a shape of an ultra-high-molecular-weight polyethylene microporous membrane.

As an organic liquid mixture which can be separated by the present separation method, there is a mixture of a solvent which dissolves polyacrylic acid ester such as benzene, toluene, chlorinated hydrocarbon, tetrahydrofuran, and aliphatic alcohol having a carbon number of 1 to 4, and a non-solvent which does not dissolve polyacrylic acid ester such mixtures as aliphatic hydrocarbon, carbon tetrachloride, aliphatic alcohol (having 5 or more carbon atoms), cyclohexanol, tetrahydrofurfural, and the like. Besides the aforementioned benzene/cyclohexane, specific examples include benzene/n-hexane, benzene/n-heptane, toluene/cyclohexane, toluene/methylcyclohexane,

hexane/heptane, toluene/benzene, benzene/water and the like. These mixtures may be not only the aforementioned bicomponent system, but also polycomponent of tricomponent or more.

[Examples]

The present invention will be described in more detail by way of specific Examples.

Example 1

An ultra-high-molecular-weight polyethylene microporous membrane (manufactured by Tonen Sekiyukagaku Co., Ltd.) having a weight average molecular weight of  $25 \times 10^5$ , a membrane thickness of 10  $\mu\text{m}$ , a porosity of 70%, an average pore diameter of 0.02  $\mu\text{m}$  and a break strength of 4700  $\text{kg}/\text{cm}^2$  was irradiated with plasma using a plasma polymerization apparatus (manufactured by Samuko Co., Ltd.). The conditions of plasma treatment thereupon are shown in Table 1.

Table 1.

High frequency output	10 W
Plasma irradiation time	60 seconds
Atmosphere	Argon
Atmosphere pressure	0.1 mbar

Then, the plasma-treated ultra-high-molecular-weight polyethylene microporous membrane was immersed into 4% by volume of an aqueous methyl acrylate solution for 15

minutes. A temperature of the aqueous solution at immersion was 30°C.

After immersion, the ultra-high-molecular-weight polyethylene microporous membrane was washed in toluene over night, and dried at room temperature. After drying, a weight of the membrane was measured, and a graft polymerization amount was determined by a change from the membrane of initial weight. A polymerization weight was 2.3 mg/cm<sup>2</sup>.

ATR of the resulting membrane was measured, and it was confirmed that a material formed on the ultra-high-molecular-weight polyethylene microporous membrane was polymethyl acrylate.

Using this separation membrane, experiment of separating a benzene/cyclohexane mixed solution was performed by pervaporization. A temperature of a supply solution (benzene/cyclohexane mixed solution: benzene concentration (weight ratio) 0.5) was set at 25°C, 40°C, 50°C and 60°C, and a permeation flux (Q) and a separation coefficient ( $\alpha$ ) thereupon were obtained. The results are shown in Fig. 2.

#### Example 2

According to the same manner as that of Example 1, a separation membrane was formed in which methyl acrylate was graft-polymerized on an ultra-high-molecular-weight polyethylene microporous membrane.

A temperature of a supply solution

(benzene/cyclohexane mixed solution) was set at 50°C, the concentration (weight ratio) of benzene in the mixed solution was set at 0.2 to 0.9, and separation experiment was performed by a pervaporization method. A weight ratio of benzene in a gas which had permeated through the separation membrane was obtained. The results are shown in Fig. 3. A permeation flux ( $Q$ ) and a separation coefficient ( $\alpha$ ) thereupon were obtained. The results are shown in Fig. 4.

As seen from the foregoing, the separation membrane of the present invention selectively makes benzene among a benzene/cyclohexane mixed solution permeate over a wide range of a concentration and a temperature. In particular, at a temperature of a supply solution of 25°C, a separation coefficient shows an extremely high value as 14.8.

#### [Effect of the Invention]

The separation membrane of the present invention uses, as a substrate, an ultra-high-molecular-weight polyethylene microporous membrane, has the favorable swelling resistance in an organic solvent, and is excellent in the mechanical strength and the durability.

In addition, in the separation membrane of the present invention, since an acrylic polymer substantially chokes the interior of a pore of a microporous membrane, an organic substance having the affinity with a graft polymer can be separated with high selectivity by using a pervaporization method or a reverse osmosis method. In

particular, when a separation membrane obtained by graft-polymerizing a methyl acrylate monomer is used, a solvent can be selectively separated from a mixed solution of a solvent which dissolves polyacrylic acid such as benzene, toluene, chlorinated hydrocarbon, tetrahydrofuran and the like, and a non-solvent which does not dissolve polyacrylic acid such as aliphatic hydrocarbon, carbon tetrachloride and the like. In particular, benzene can be selectively separated from a benzene/cyclohexane mixed solution.

Since the separation membrane of the present invention uses a microporous membrane of ultra-high-molecular-weight polyethylene as a substrate, a uniform and reproducible separation membrane is easily obtained, being preferable.

Such the separation membrane is suitably used in separating an organic solvent mixture by a pervaporization method or a reverse osmosis method and, in particular, is useful for separating a benzene/cyclohexane mixture.

#### 4. Brief Description of the Drawings

Fig. 1 is a schematic cross-sectional view conceptionally showing a step of plasma graft-polymerizing an acrylic monomer on an ultra-high-molecular-weight polyethylene microporous membrane, (a) represents an ultra-high-molecular-weight polyethylene microporous membrane, and (b-1) and (b-2) represent graft-polymerized ultra-high-molecular-weight polyethylene microporous membrane, respectively.

Fig. 2 is a graph showing the relationship between a temperature of a benzene/cyclohexane mixed solution, a permeation flux ( $Q$ ) and a separation coefficient ( $\alpha$ ), when benzene is separated from a benzene/cyclohexane mixed solution by a pervaporization method using the separation membrane of one Example of the present invention.

Fig. 3 is a graph showing the relationship between the concentration of benzene in a benzene/cyclohexane mixed solution to be separated, and a weight ratio of benzene in a substance which has permeated through a separation membrane.

Fig. 4 is a graph showing the relationship between the concentration of benzene in a benzene/cyclohexane mixed solution to be separated, a permeation flux ( $Q$ ) and a separation coefficient ( $\alpha$ ).